Theor Chem Acc (2006) 115: 334–342
DOI 10.1007/s00214-005-0060-6

REGULAR ARTICLE

Federico Moscardó · Emilio San-Fabián
Luis Pastor-Abia

The Colle–Salvetti wavefunction revisited: a comparison between three approaches for obtaining the correlation energy

Received: 20 July 2005 / Accepted: 28 September 2005 / Published online: 2 February 2006

Abstract The correlation factor of Colle and Salvetti is studied by comparing the behavior of three different correlation functionals. The normalization, sum rule, Coulomb hole, correlation energy integrand, and the Wigner exclusion hole have all been analyzed by applying the three approaches. The results indicate that the correlation factor proposed by Colle–Salvetti is a very good choice for modeling electron correlation in atoms. The flaws appearing in the development of the Colle–Salvetti equations seem mainly due to an inadequate use of the first mean value theorem of integral calculus. The Gaussian summation used for the two-body density matrix seems to be a good approximation to obtain the correlation factor equations.

Keywords Correlation energy · Correlation factor · Correlated wavefunction

1 Introduction

The Colle and Salvetti (CS) functional [1,2] is one of the most celebrated formulas for the approximate estimation of the correlation energy of atoms and molecules. It is not rigorously a functional of the density, but, by departing from it, Lee, Yang, and Parr (LYP) [3] wrote an expression as a density functional, related to a wavefunction written as a Slater determinant, no matter it be of Kohn Sham or Hartree–Fock (HF) class. The LYP is, by far, the most widely used correlation energy functional for atoms' and molecules' calculations, and all the acronyms including it, such as BLYP, etc., are nowadays very popular in quantum chemistry.

Despite its success in density functional theory (DFT) calculations, the CS functional shows its power when a wavefunction having more than a Slater determinant is applied to the estimation of correlation energy. Instead, the DFT-based correlation energy functionals, including that of LYP, do not work for such a many determinantal wavefunction [4–6]. This fact hints towards the inclusion of a dependence on the reduced two-body density matrix (RTBDM) into the DFT correlation energy functionals. This is accomplished by relating the components of the density with the on-top two body density [7], and has been shown to be a powerful tool in molecular calculations [8].

Although the CS functional has been widely applied in a direct or indirect way (the paper "Development of the Colle-Salvetti correlation energy formula into a functional of the electron density" [3] alone has received more than 12,000 citations), it is less known from theoretical grounds. The functions $\beta(\mathbf{R})$, $\Phi(\mathbf{R})$, and $\varphi(\mathbf{R}, \mathbf{r})$ appearing in the CS wavefunction, were studied in Ref. [9]. A correlation coefficient for the CS wavefunction was analyzed in Refs. [10,11]. The application to a homogeneous electron gas was done by Mc. Weeny and coworkers [12]. The correlation energy potential has been carefully analyzed [13]. Recently, the correlation hole, sum rule, correlation energy density, and electrostatic potential have been also studied [14,15]. From these studies it follows that some important flaws are found in the CS formalism, casting serious doubts on the physical meaning of the CS wavefunction, despite the good results provided by the CS functional for the correlation energy of atoms and molecules.

Our aim in this paper is to elucidate the wrong behavior of the CS wavefunction when describing some physical and mathematical properties of atoms and molecules. For this purpose a comparative analysis is made by using together the CS formalism, a correlation energy functional due to Moscardó and San-Fabián (MSF) [17] and a more recent functional by Salvetti and Montagnani (SM) [16].

2 Theory

2.1 Colle–Salvetti correlation factor

The CS wavefunction is a Jarstrow class [18] written as

F. Moscardó (✉) · E. San-Fabián · L. Pastor-Abia
Departamento de Química Física,
Universidad de Alicante,
Apartado 99, 03080 Alicante, Spain
E-mail: moscardo@ua.es, sanfa@ua.es

$$\Psi(\mathbf{x_1}, \mathbf{x_2}, \ldots, \mathbf{x_n}) = \Psi^0(\mathbf{x_1}, \mathbf{x_2}, \ldots, \mathbf{x_n}) \times \Pi_{ji}[1 - \varphi(\mathbf{r_i}, \mathbf{r_j})] \quad (1)$$

where Ψ^0 is a known reference wavefunction, usually an HF class, and $\mathbf{x_i}$ is the set of space ($\mathbf{r_i}$) and spin coordinates for the i-electron.

By invoking the first mean value theorem of integral calculus [19] [see Eq. (36)] CS puts forward

$$\Gamma_2(\mathbf{r_1}, \mathbf{r_2}; \mathbf{r'_1}, \mathbf{r'_2}) = \Gamma_2^0(\mathbf{r_1}, \mathbf{r_2}; \mathbf{r'_1}, \mathbf{r'_2}) \, [1 - \varphi(\mathbf{r_1}, \mathbf{r_2}) - \varphi^*(\mathbf{r'_1}, \mathbf{r'_2}) + \varphi(\mathbf{r_1}, \mathbf{r_2})\varphi^*(\mathbf{r'_1}, \mathbf{r'_2})\big] \quad (2)$$

for the RTBDM. $\Gamma_2^0(\mathbf{r_1}, \mathbf{r_2}; \mathbf{r'_1}, \mathbf{r'_2})$ is the reference RTBDM, and φ is a space correlation function

$$\varphi(\mathbf{r_1}, \mathbf{r_2}) = e^{-\beta^2 r^2} \left[1 - \Phi(\mathbf{R}) \left(1 + \frac{r}{2}\right)\right] \quad (3)$$

where $\mathbf{R}$ and $\mathbf{r}$ are the center of mass and internal vectors

$$\mathbf{R} = \frac{(\mathbf{r_1} + \mathbf{r_2})}{2} \qquad \mathbf{r} = (\mathbf{r_1} - \mathbf{r_2}) \quad (4)$$

When we are restricted, as in this paper, to the Helium atom, Eq. (2) follows exactly from Eq. (1). However, for many electron systems the use of Eq. (2) may have serious consequences affecting the N-representability. This problem has been discussed by Soirat et al. [20], proposing a correction to Eq. (2) that is exact to an order of two.

Turning to Eq. (3), it depends on the function β that, following the concept of Wigner exclusion hole [21], CS fixes as

$$\beta(\mathbf{R}) = q\rho(\mathbf{R})^{1/3} \quad (5)$$

Here q is a parameter related with the mass of electrons into the correlation hole, and $\rho(\mathbf{R})$ is the electron density.

The other function $\Phi(\mathbf{R})$, appearing in Eq. (3), is also a function of β.

Assuming that the reduced one-electron density matrix (ROEDM) satisfies $\Gamma_1(\mathbf{r}, \mathbf{r'}) = \Gamma_1^0(\mathbf{r}, \mathbf{r'})$, a sum rule for the correlation hole holds

$$\int \Gamma_2^0(\mathbf{r_1}, \mathbf{r_2}; \mathbf{r_1}, \mathbf{r_2}) \left[\varphi^2(\mathbf{r_1}, \mathbf{r_2}) - 2\varphi(\mathbf{r_1}, \mathbf{r_2})\right] \mathrm{d}\mathbf{r_2} = 0 \quad (6)$$

suggesting the expression

$$\int \Gamma_2^0(\mathbf{R}, \mathbf{r}; \mathbf{R}, \mathbf{r}) \left[\varphi^2(\mathbf{R}, r) - 2\varphi(\mathbf{R}, r)\right] \mathrm{d}\mathbf{r} = 0 \quad (7)$$

In a similar way a correlation energy can be written as

$$E_c = \int \frac{1}{2} \Gamma_2^0(\mathbf{R}, \mathbf{r}) \frac{\varphi^2(\mathbf{R}, r) - 2\varphi(\mathbf{R}, r)}{r} \mathrm{d}\mathbf{R}\mathrm{d}\mathbf{r} \quad (8)$$

From Eq. (7), and following an empirical reasoning, CS arrives at

$$\Phi_{\mathrm{CS}}(\mathbf{R}) = \frac{\pi^{1/2}\beta(\mathbf{R})}{1 + \pi^{1/2}\beta(\mathbf{R})} \quad (9)$$

Moreover, this Eq. (9) can also be derived from Eq. (7). So, neglecting the φ^2 contribution

$$\int \Gamma_2^0(\mathbf{R}, \mathbf{r}; \mathbf{R}, \mathbf{r}) \, [\varphi(\mathbf{R}, r)] \, \mathrm{d}\mathbf{r} = 0 \quad (10)$$

and invoking the mean value theorem [see Eq. (36)]

$$\Gamma_2^0(\mathbf{R}, \xi; \mathbf{R}, \xi) \int \varphi(\mathbf{R}, r) \mathrm{d}\mathbf{r} = 4\pi \int r^2 e^{-\beta^2 r^2} \left[1 - \Phi(\mathbf{R}) \left(1 + \frac{r}{2}\right)\right] \mathrm{d}r = 0 \quad (11)$$

so, by integration of this equation, we arrive at the $\Phi_{\mathrm{CS}}(\mathbf{R})$ expression.

In the CS paper the integrand of Eq. (8) is approximated by a function also built on empirical grounds:

$$H(\mathbf{R}) = 0.04918 \times \frac{1{+}0.173 \left[0.3814\rho(\mathbf{R})^{-8/3} \left(\nabla_r^2 \rho_2^0(\mathbf{R} - \mathbf{r}/2; \mathbf{R} - \mathbf{r}/2)\right)_{r=0}\right] e^{-0.58/\beta}}{1 + 0.8/\beta} \rho(\mathbf{R}) \quad (12)$$

2.2 Moscardó–San-Fabián equations

In Refs. [16,22], a model derived from that of Colle–Salvetti was proposed. The starting equation is not a correlated wavefunction, but a directly correlated RTBDM

$$\Gamma_2(\mathbf{r_1}, \mathbf{r_2}; \mathbf{r'_1}, \mathbf{r'_2}) = \Gamma_2^0(\mathbf{r_1}, \mathbf{r_2}; \mathbf{r'_1}, \mathbf{r'_2}) \times [1 + F(\mathbf{r_1}, \mathbf{r_2}; \mathbf{r'_1}, \mathbf{r'_2})] \quad (13)$$

where $F(\mathbf{r_1}, \mathbf{r_2}; \mathbf{r'_1}, \mathbf{r'_2})$ is a correlation factor having the following properties:

$$F(\mathbf{r_1}, \mathbf{r_2}; \mathbf{r'_1}, \mathbf{r'_2}) = F^*(\mathbf{r_1}, \mathbf{r_2}; \mathbf{r'_1}, \mathbf{r'_2}) = F(\mathbf{r'_1}, \mathbf{r'_2}; \mathbf{r_1}, \mathbf{r_2}) \quad (14)$$

and

$$F(\mathbf{r_1}, \mathbf{r_2}; \mathbf{r'_1}, \mathbf{r'_2}) \geq -1 \quad (15)$$

With these definitions the possible difficulties related with a loss of n-representability when going from Eq. (1) to Eq. (2) are overcome[1].

As in CSs paper, a cusp condition on the RTBDM is imposed

$$\left.\frac{\partial \overline{F}(\mathbf{R}, r)}{\partial \mathbf{r}}\right|_{r=0} = 1 \quad (16)$$

where $\overline{F}(\mathbf{R}, r)$ is the angular average of $F(\mathbf{R}, \mathbf{r})$.

In Ref. [16] the averaged correlation factor is taken as

$$\overline{F}(\mathbf{R}, r) = \varphi^2(\mathbf{R}, r) - 2\varphi(\mathbf{R}, r) \quad (17)$$

where $\varphi(\mathbf{R}, r)$ is that of Eq. (3), and the same transformation of coordinates of Eq. (4) is used. Hence, Eqs. (7) and (8) remain to be valid in this derivations.

---

[1] These are necessary but no sufficient conditions. For a more deeper analysis on the N-representability of the reduced density matrices see the papers of Valdemoro [23,24], Ehara et al. [25], and Mazziotti [26, 27]

Another remarkable feature of the model is the use of a Gaussian summation to substitute the second-order Taylor development made in the CS paper [1]. In this way the divergences and false zeros appearing in the CS equations are not present here. The spherically averaged reference RTBDM is approximated by

$$\overline{\Gamma_2^0}(\mathbf{R}, r) = \int \Gamma_2^0(\mathbf{R}, \mathbf{r}) \mathrm{d}\Omega = 4\pi \rho_2^0(\mathbf{R}) e^{-r^2/\gamma(\mathbf{R})} \tag{18}$$

where Ω stand for the set of polar angles defining the vector $\mathbf{r}$, and $\rho_2^0(\mathbf{R})$ is the on-top diagonal RTBDM.

Further, an explicit expression for $\gamma(\mathbf{R})$ is obtained

$$\gamma(\mathbf{R}) = \frac{1}{\pi}\left[\frac{(N-1)}{2}\frac{\rho^0(\mathbf{R})}{\rho_2^0(\mathbf{R})}\right]^{2/3} \tag{19}$$

by imposing that the hierarchy relation between the reduced two- and one-body density matrices be also obeyed by integration on the internal coordinates.

$$\rho^0(\mathbf{R}) = \frac{2}{N-1}\int_0^\infty \overline{\Gamma_2}(\mathbf{R}, r) r^2 \mathrm{d}r \tag{20}$$

Integration of Eq. (7), using the Eq. (18), leads to

$$\Phi_{\mathrm{MSF}}(\mathbf{R}) = \frac{(C_2^2 + 4C_1C_3)^{1/2} - C_2}{2C_1} \tag{21}$$

with

$$C_1 = \frac{\sqrt{\pi}}{2a^{3/2}}\beta^2(\mathbf{R}) + \frac{\beta(\mathbf{R})}{a^2} + \frac{3\sqrt{\pi}}{16a^{5/2}}$$

$$C_2 = \sqrt{\pi}\left(\frac{1}{b^{3/2}} - \frac{1}{a^{3/2}}\right)\beta(\mathbf{R})^2 + \left(\frac{1}{b^2} - \frac{1}{a^2}\right)\beta(\mathbf{R})$$

$$C_3 = \sqrt{\pi}\left(\frac{1}{b^{3/2}} - \frac{1}{2a^{3/2}}\right)\beta(\mathbf{R})^2$$

$$a = 2 + \frac{\rho^0(\mathbf{R})^{2/3}}{t\beta^2(\mathbf{R})} \qquad b = a - 1$$

$$t = \frac{(N-1)^{2/3}}{\pi}\left[\frac{\rho^0(\mathbf{R})^2}{\rho_2^0(\mathbf{R})}\right]^{2/3}$$

Finally, a correlation energy functional is obtained from Eq. (8)

$$E_c = \int \varepsilon_c(\mathbf{R}) \mathrm{d}\mathbf{R} \tag{22}$$

where the pair correlation energy density $\varepsilon_c(\mathbf{R})$ is

$$\begin{aligned}\varepsilon_c(\mathbf{R}) = {} & \frac{2(N-1)}{\pi^{1/2}}\frac{\rho^0(\mathbf{R})^2}{\beta^4 t^{3/2}} \\ & \times \left\{\phi^2(\mathbf{R})\left(\frac{\beta^2}{2a} + \frac{\alpha\beta\pi^{1/2}}{2a^{3/2}} + \frac{\alpha^2}{2a^2}\right)\right. \\ & + \phi(\mathbf{R})\left[\left(\frac{1}{b} - \frac{1}{a}\right)\beta^2 + \frac{\alpha\pi^{1/2}}{2}\left(\frac{1}{b^{3/2}} - \frac{1}{a^{3/2}}\right)\beta\right] \\ & \left. - \left(\frac{1}{b} - \frac{1}{2a}\right)\beta^2\right\}\end{aligned} \tag{23}$$

With the objective to test the mean value theorem used by Colle–Salvetti to obtain Φ, we can use the Gaussian summation. Neglecting the φ^2 contribution in Eq. (7), it is easy to obtain an approximation to the Eq. (21), equivalent to that of CS [see Eq. (9)] but without invoking the mean value theorem:

$$\Phi_{\mathrm{AGS}} = \frac{\pi^{1/2}\sqrt{\delta(\mathbf{R})}}{1 + \pi^{1/2}\sqrt{\delta(\mathbf{R})}} \tag{24}$$

with

$$\delta(\mathbf{R}) = \beta^2 + \gamma(\mathbf{R})^{-1}$$

2.3 Salvetti–Montagnani equations

More recently Salvetti and Montagnani have proposed a new functional for the exchange plus correlation energy [17]. The aim of this functional is to overcome some difficulties appearing in the CS one [1] and is inspired in it, although there are important differences that make both not so similar.

As in Ref. [16], the starting point is a correlated RTBDM

$$\rho_2(\mathbf{r_1}, \mathbf{r_2}) = \rho(\mathbf{r_1})\rho(\mathbf{r_2})[1 + h(\mathbf{r_1}, \mathbf{r_2})] \tag{25}$$

where the $\rho_2(\mathbf{r_1}, \mathbf{r_2})$ and $\rho(\mathbf{r_i})$ are the diagonal-reduced two- and one-body density matrices, respectively, and $h(\mathbf{r_1}, \mathbf{r_2})$ is an exchange-correlation factor written as

$$h(\mathbf{r_1}, \mathbf{r_2}) = \frac{\varphi_{\mathrm{SM}}^2 - 2\varphi_{\mathrm{SM}}}{f} \tag{26}$$

where

$$\varphi_{\mathrm{SM}} = \Phi_{\mathrm{SM}} e^{-\beta_{\mathrm{SM}} r^2}\left[1 - \Phi_{\mathrm{SM}}(1 + \frac{r}{2})\right] \tag{27}$$

f is a polynomial function of Φ_{SM}, and

$$\Phi_{\mathrm{SM}} = \frac{\beta_{\mathrm{SM}}^\mu}{1 + \beta_{\mathrm{SM}}^\mu} \tag{28}$$

with

$$\beta_{\mathrm{SM}}(\mathbf{r_1}, \mathbf{r_2}) = \lambda\rho(\mathbf{r_1})^{1/3}\rho(\mathbf{r_2})^{1/3} \tag{29}$$

The sum rule for the exchange correlation hole is imposed:

$$\int \rho(r_2) h(r_1, r_2) \mathrm{d}r_2 = -1 \tag{30}$$

Equations (27) and (28) resemble those of CS [Eqs. (3), (5), and (9) of this paper]; however, there are deep differences between them; so, it is not possible to go from Eq. (27) to (3), and Eq. (9) is not recoverable from Eq. (28).

3 Two-electron system

3.1 Sum rule

As has been pointed in Sect. 2, all the results following are for the ground state of the helium atom. The reference

Table 1 Value of $\int \Gamma_2^{\mathrm{HF}}(r_1, r_2; r_1, r_2)(2\varphi - \varphi^2)d\mathbf{r_2}d\mathbf{r_1}$ versus q, using the Φ_{CS}, Φ_{MSF}, and Φ_{AGS} functions

q	Φ_{CS}	Φ_{MSF}	Φ_{AGS}	q	Φ_{CS}	Φ_{MSF}	Φ_{AGS}
0.25	1.61863	−0.10399	−0.15001	2.25	0.02641	0.00400	0.00241
0.50	1.04280	−0.04203	−0.07314	2.29	0.02458	0.00385	0.00235
0.75	0.61355	−0.00759	−0.02733	2.50	0.01722	0.00316	0.00201
1.00	0.35013	0.00514	−0.00694	2.75	0.01151	0.00245	0.00159
1.17	0.23862	0.00737	−0.00147	3.00	0.00791	0.00193	0.00146
1.25	0.19965	0.00800	0.00033	3.25	0.00562	0.00150	0.00104
1.50	0.11528	0.00753	0.00252	3.50	0.00401	0.00119	0.00083
1.75	0.06839	0.00638	0.00290	3.75	0.00286	0.00093	0.00066
1.80	0.06195	0.00592	0.00311	4.00	0.00213	0.00073	0.00051
2.00	0.04204	0.00538	0.00279	5.00	0.00073	0.00032	0.00023

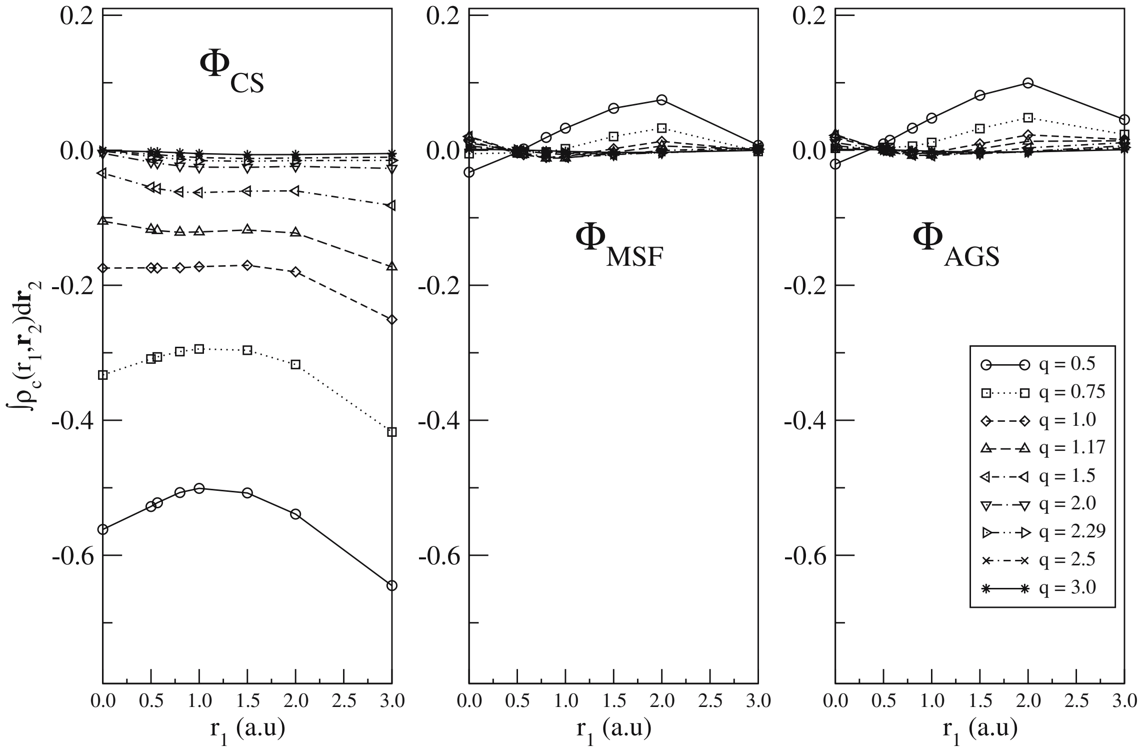

Fig. 1 $\int \rho_c(\mathbf{r_1}, \mathbf{r_2})d\mathbf{r_2}$ [Eq.(31)] versus r_1, for Φ_{CS}, Φ_{MSF}, and Φ_{AGS} [Eqs. (9), (21), and (24) respectively]

wavefunction is a Hartree–Fock one built from an augmented correlation consistent valence quintuple zeta (aug-cc-pV5Z) Dunning's basis set, excluding g and h shells [28,29], and the integration has been done by numerical quadrature.

The Table 1 shows the values obtained by complete integration of Eq. (6). The results of the first column are equal as those of Ref. [14], so that, when Eq. (9) is used, the normalization of the CS wavefunction is strongly dependent on the q value. Only for high values of q the zero is reasonably approached. When Φ_{MSF} is used, the integral value is approximately zero for all the rank of q's, only for very small q the result deviate from zero, probably due to the Gaussian approximation.

The results collected in the last column of Table 1 are very similar to those of the second column, making it evident that the functions Φ_{MSF} and Φ_{AGS} works in the same way. Remember that the only difference in obtaining both equations is the neglect of the φ^2 contribution in Eq. (7).

The above results shows that the use of a Gaussian summation for the power series development around r of the reference RTBDM seems to be a good approximation.

3.2 Coulomb hole

From Eq. (2) a Coulomb hole can be written as

$$\rho_c(\mathbf{r_1}, \mathbf{r_2}) = \frac{\Gamma_2^0(\mathbf{r_1}, \mathbf{r_2})\left[\varphi^2(\mathbf{r_1}, \mathbf{r_2}) - 2\varphi(\mathbf{r_1}, \mathbf{r_2})\right]}{\rho^0(\mathbf{r_1})} \tag{31}$$

where $\rho^0(\mathbf{r_1})$ is the reference density.

Results of integration of Eq. (31) on $\mathbf{r_2}$ are shown in Fig. 1, these are curves depending on r_1, and parametrically on q. If

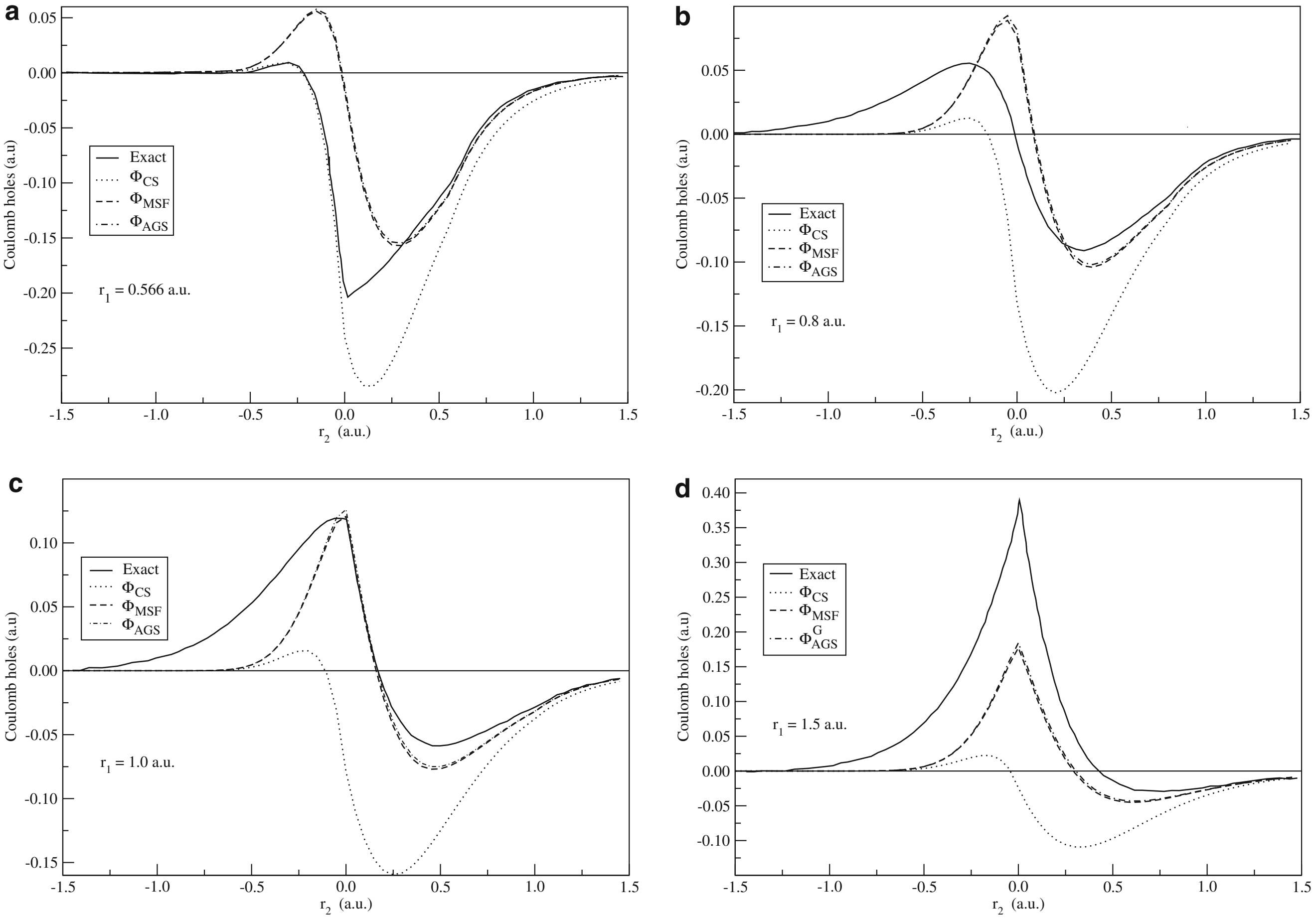

Fig. 2 Plot of the Coulomb hole through the z axis, using $q = 1.17$. The exact curves are those obtained by Slamet and Sahni [30]

the sum rule of Eq. (6) would be obeyed, all the curves must be superposed along the abscissas axis. However, the curves associated to the Φ_{CS} function exhibits a strong dependence on q, and are not linear in r_1. On the contrary, curves associated to Φ_{MSF} and Φ_{AGS} are less dependent on q being grouped around the zero value. An exception is the curves for $q = 0.5$.

The Coulomb hole along the z axis, together with the exact one of (Ref. [30]), for different r_1 values (0.566, 0.8, 1.0, and 1.5 Å), are shown in Fig. 2. All them are obtained with $q = 1.17$, the variational value found in Ref. [20]. Such as has been previously pointed by Singh et al. [14], when the test electron moves to outer regions, the CS Coulomb hole becomes worse. Contrarily, the MSF and AGS Coulomb holes maintain for all the range of r_1 distances, a good resemblance to the exact ones, showing that, not only short range correlations but also long range ones are reasonably well depicted by the MSF or AGS Coulomb holes.

3.3 Correlation energy

The correlation energy density per electron is shown in Fig. 3. The $\varepsilon^{(1)}_{\mathrm{CS}}$, and $\varepsilon^{(1)}_{\mathrm{MSF}}$ are obtained dividing by $\rho(\mathbf{R})$ the integrand of Eqs. (12) and (23), respectively; $\varepsilon^{(2)}_{\mathrm{CS}}$, $\varepsilon^{(2)}_{\mathrm{MSF}}$, and $\varepsilon^{(2)}_{\mathrm{AGS}}$, are

$$\varepsilon_k^{(2)} = \int \frac{1}{2}\frac{\Gamma_2^0(\mathbf{R},\mathbf{r})}{\rho(\mathbf{R})}\frac{\varphi_k^2(\mathbf{R},r) - 2\varphi_k(\mathbf{R},r)}{r}\mathrm{d}\mathbf{r} \qquad (32)$$

where k means that Φ_{CS}, Φ_{MSF} or Φ_{AGS} is used to write $\varphi_k(\mathbf{R}, r)$, respectively.

The RTBDM in Eq. (8) is that of Hartree–Fock:

$$\Gamma_2^0(\mathbf{r},\mathbf{r}') = \rho^0(\mathbf{r})\rho^0(\mathbf{r}') - \frac{1}{2}\sum_i\sum_j \phi_i^0(\mathbf{r})\phi_j^0(\mathbf{r})\phi_i^0(\mathbf{r}')\phi_j^0(\mathbf{r}') \qquad (33)$$

More interesting than Fig. 3 are the values of q needed for each of the four integrands to yield the exact ground state correlation energy of the Helium atom (−0.042 Å). These values are 2.29, 2.29, 1.80, 1.70, and 1.64 for $\varepsilon^{(1)}_{\mathrm{CS}}$, $\varepsilon^{(2)}_{\mathrm{CS}}$, $\varepsilon^{(1)}_{\mathrm{MSF}}$, $\varepsilon^{(2)}_{\mathrm{MSF}}$, and $\varepsilon^{(2)}_{\mathrm{AGS}}$, respectively, and they have been employed in the previous calculations. In Ref. [1], Colle and Salvetti define an exclusion volume around an electron as

$$V_c = \int e^{-\beta^2 r^2}\mathrm{d}\mathbf{r} = \frac{\pi^{3/2}}{\beta^3} \qquad (34)$$

where β is that of Eq. (5).

According to the model, the electron mass into the hole is $m = \pi^{3/2}/q^3$, and if any other electron must be expelled out of the hole, this mass would be equal to 1. This implies a

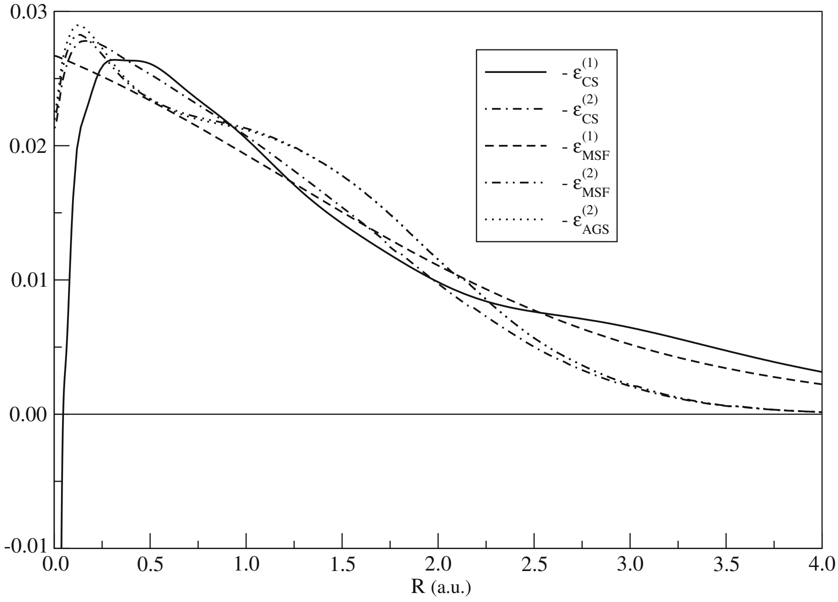

Fig. 3 Correlation energy per electron (a.u.), as a function of R

$q = 1.77$, very near to the values for $\varepsilon^{(1)}_{\mathrm{MSF}}$, $\varepsilon^{(2)}_{\mathrm{MSF}}$, and $\varepsilon^{(2)}_{\mathrm{AGS}}$. The $\varepsilon^{(1)}_{\mathrm{CS}}$ and $\varepsilon^{(2)}_{\mathrm{CS}}$ show a hole having a defect of about half electron.

3.4 Gaussian approximation

Plots along the z axis, for the reference RTBDM of Eq. (33) and its Gaussian approximation [Eq. (18)], are shown in Fig. 4. Each curve is for a fixed r, and shows the pair probability as a function of R. Both functions exhibit a very similar shape. At short inter electron distances the curves are nearly superposed, but when r increases, the Gaussian curve concentrates around the origin, and the area within it decreases more quickly than that for the RTBDM of Eq. (33). This figure suggests that the Gaussian RTBDM is a reasonable approximation for the reference RTBDM, having a very good behavior in the region of short correlations.

3.5 Mean value theorem

The only approximation used to integrate the equations appearing in the Salvetti and Montagnani paper [17] is that they use the first mean value theorem of integral calculus [19]. Consequently, the analysis of these equations can help the present study. The f function of Eq. (26), was introduced in Ref. [17] to guarantee the sum rule for the exchange correlation hole [Eq. (30)].

In obtaining the Eq. (11) of Ref. [17], only the mean value theorem is invoked, hence by using this equation for the exact numerical integration of the left hand of Eq. (30), it is possible to have direct information about the goodness of the mean value theorem application to this class of integrals. Table 2 shows, for a set of values of r_1, the result of the integration. If the f function were the exact one, the integral must have a constant value of -1; instead, the results exhibit a strong dependency on r_1, whit values that change in a broad range.

The f function of Eq. (11) of Ref. [17] was obtained by assuming that there is only a point (ε, τ), where the mean value theorem holds, and taking it as the point (0,0). To test this assumption, we have searched for sets of points (ε, τ) leading to the equality of Eq. (30). With this aim, two new β_{SM} functions are obtained for each couple of values ε, τ:

$$\begin{aligned} \beta_{\mathrm{SM}}(\mathbf{r_1}, \varepsilon) &= \lambda\rho(\mathbf{r_1})^{1/3}\rho(\varepsilon)^{1/3} \\ \beta_{\mathrm{SM}}(\mathbf{r_1}, \tau) &= \lambda\rho(\mathbf{r_1})^{1/3}\rho(\tau)^{1/3} \end{aligned} \tag{35}$$

The first of them is to be included into the Φ_{SM} function of Eq. (27), the other is used in evaluating the a_j coefficients appearing in Eq. (11) of Ref. [17].

Figure 5 shows that the paths along the equality of Eq. (30) is satisfied; it appears a variety of curves depending on the value taken for r_1, hence the condition that Eq. (30) must hold independently of r_1, is not fulfilled by the f function proposed by Salvetti and Montagnani [17].

4 More than two-electron atoms

Equation (2) is exact only for a two-electron system, such as the helium atom; but for the N-representability to be satisfied by the TBDM of a many-electron system, Eq. (2) must be adequately corrected (see the second-order term in the work of Soriat et al. [20]). By invoking the mean value theorem, in the Colle and Salvetti work this correction is put to zero, and Eq.(2) is taken for any N-electron TBDM. Tests on atoms other than helium can aid to show the validity of this hypothesis.

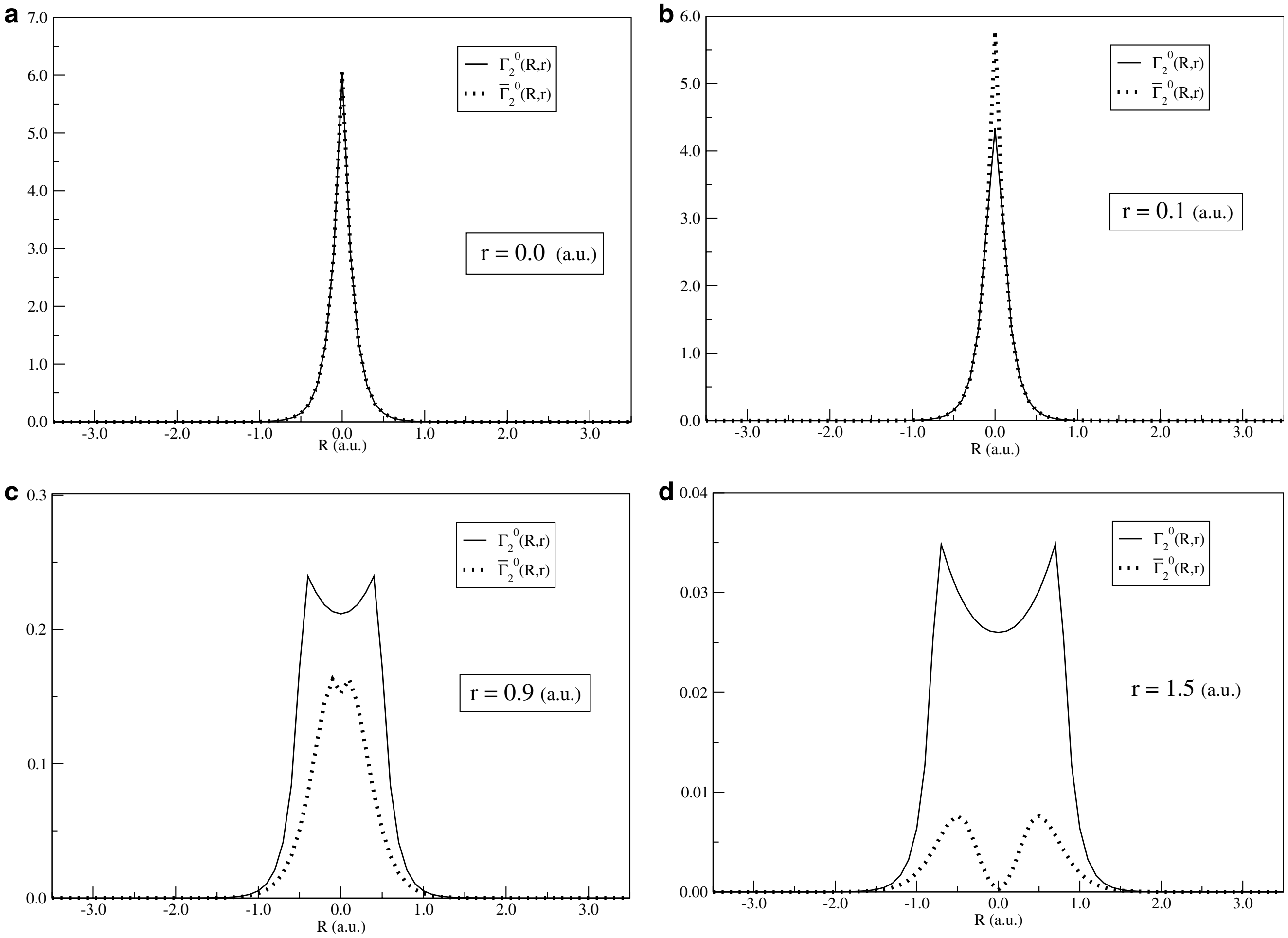

Fig. 4 Comparison of $\Gamma_2^0(R, r)$ and its Gaussian summation functions, along R axis, for constant values of interelectronic distances r

Table 2 Normalization sum rule for the Salvetti–Montagnani exchange-correlated hole ($I_{xc} = \int \rho(\mathbf{r_2})h(\mathbf{r_1}, \mathbf{r_2})d\mathbf{r_2}$). The λ and μ parameters of Eqs. (26) and (27) are those found in Ref. [17] ($\lambda = 1.62$ and $\mu = 0.46$)

r_1 (Å)	0.0001	0.5	0.566	0.8	1.0	1.5	2.0	3.0	4.0	5.0	6.0
I_{xc}	−0.44949	−0.57658	−0.57880	−0.57616	−0.56939	−0.56352	−0.59060	−0.75074	−1.01704	−1.41849	−1.98212

Figure 6 shows, for the ground state of beryllium atom, the values taken by the sum rule integral [Eq. (6)] versus the q value, when the Φ_{CS}, Φ_{MSF}, and Φ_{AGS} are used. For comparison purposes, the helium results of Table 1 are also shown. The reference wavefunction used for the beryllium atom is a restricted HF, built with the cc-pV5Z Dunning's basis set, excluding g and h shells [28,29].

The relationships appearing between the results obtained by using the Eqs. (9), (21), and (24) for the helium atom are maintained when going to the beryllium one, but the new curves deviate more from the exact one than those corresponding to Helium atom calculations. This worsening is greater for the region of $q < 1$, but in this range of values, the model losses its physical sense. For values of q bigger than $q = 1.77$ (corresponding to a correlation hole having one electron), all the curves of Fig. 6 adjust fairly well to the exact value of the sum rule integral.

The characteristics of the results discussed for the ground state of the beryllium atom, are maintained for a ten-electron system, such as the ground state of neon atom. The results for this atom are not shown here, because for little q values the scale in Fig. 6 is not so adequate to be represented together with those of helium and beryllium atoms.

5 Concluding remarks

The comparison of the CS, MSF, and SM functionals has put in evidence the origin of the flaws found in preceding papers [14,15] for the CS wavefunction [1]. The main reason is the use of the mean value theorem of integral calculus.

The Φ_{CS} function provides very bad results when applied to the sum rule, being very sensitive to the r_1 coordinate. A consequence is the loss of normalization found in Table 1.

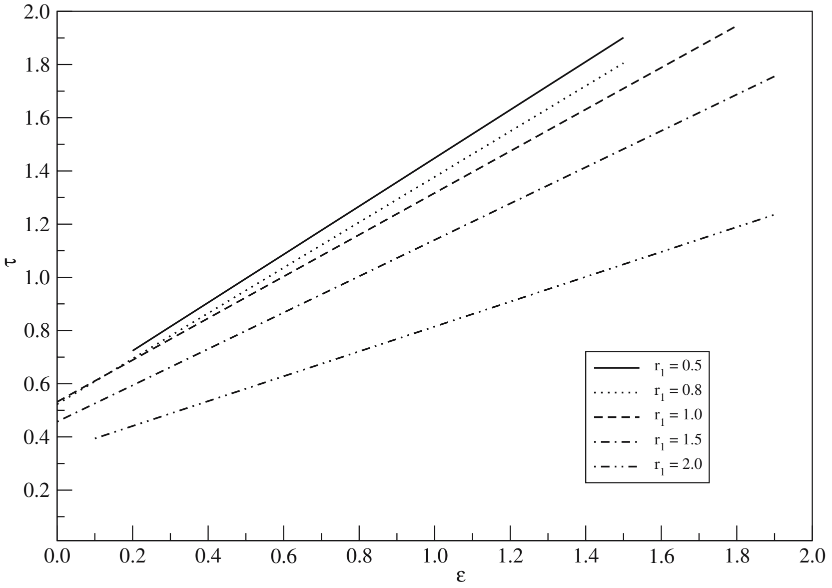

Fig. 5 Points where the condition of Eq. (30) is satisfied

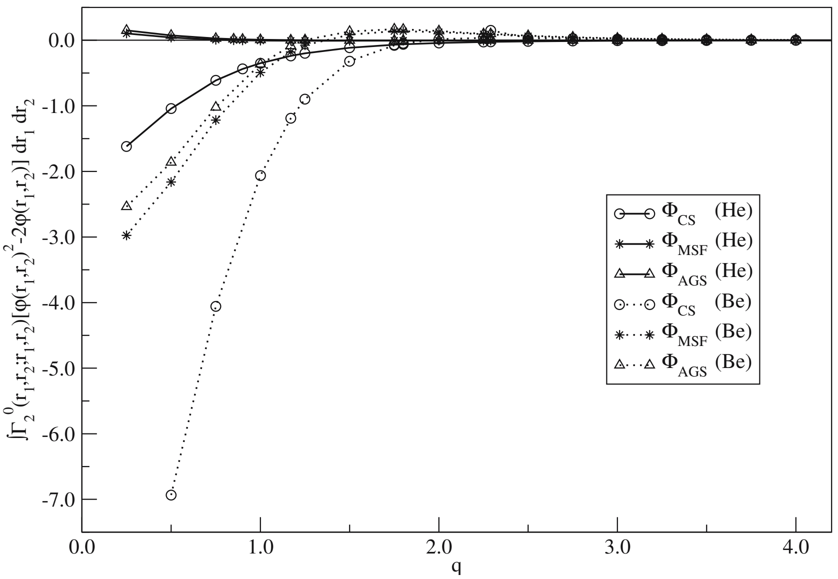

Fig. 6 Value of $\int \Gamma_2^{\mathrm{HF}}(r_1, r_2; r_1, r_2)(2\varphi(r_1, r_2) - \varphi^2(r_1, r_2))\mathbf{dr_1 dr_2}$ versus q, using the Φ_{CS}, Φ_{MSF}, and Φ_{AGS} functions, for helium and beryllium atoms

Also, the correlation hole obtained with Φ_{CS} exhibit a bad behavior, inverting the trend of the exact hole when the test electron goes to the outer regions.

The correlation energy density per electron, obtained by using Eq. (12) together with Φ_{CS}, shows an unphysical behavior near the origin, and the optimal value of q for this equation, 2.29, depicts an exclusion hole having half electron.

All these results point to the above conclusion, so that, the use of the mean value theorem seems not to be a fortunate choice for the simplification of the integrals appearing in the CS equations. This conclusion is reinforced by the analysis made on the basis of the SM equations.

The Gaussian summation seems to be a satisfactory approximation for the integrals containing the reference RTBDM. All the results found in this paper point to this conclusion. Calculations made by using Φ_{MSF}, and Φ_{AGS} lead to very similar result.

The present results for the ground state of the helium atom shows that to write $\Gamma_2(\mathbf{r_1}, \mathbf{r_2}; \mathbf{r_1'}, \mathbf{r_2'})$ using the Eq. (2) seems to be a good choice, but for a many-electron system, this equation comes from the CS wavefunction only when the mean value theorem is invoked. In view of the results found in this paper, the validity of Eq. (2) for a system having more than two electrons is a question that remains open.

Although the mean value theorem is an ingenious device to simplify the complicated integrals appearing in the CS model, its application is not so easy as it seems at the first instance. The first theorem of the mean value of integral calculus [19] states that, if $f(x)$ and $g(x)$ are integrable over $[a, b]$, if $m \leq f(x) \leq M$, if $g(x) \geq 0$ always or $g(x) \leq 0$ always, and if $f(x)$ is continuous, then there is at least one ξ with $a \leq \xi \leq b$ such that

$$\int_a^b f(x)g(x)\mathrm{d}x = f(\xi)\int_a^b g(x)\mathrm{d}x \tag{36}$$

It is easy to show that the theorem holds also for $f(x, y, \ldots)$ and $g(x, y, \ldots)$ be functions of more variables, having the same properties required above.

When the mean value theorem has been applied to the equations of this paper, some of the properties that the functions appearing in Eq. (36) must exhibit are lost. As an example we can consider the Φ_{CS}, that can be obtained form Eq. (7) by neglecting the φ^2 and then applying the mean value theorem (see Sect. 2.1). The result is

$$\begin{aligned}&\int \Gamma_2^0(\mathbf{R}, \mathbf{r})\varphi(\mathbf{R}, r)\mathrm{d}\mathbf{r}\\ &= \Gamma_2^0(\mathbf{R}, \xi)\int_0^\infty e^{-\beta^2 r^2}\left[1 - \Phi_{\mathrm{CS}}(\mathbf{R})\left(1 + \frac{r}{2}\right)\right] r^2\mathrm{d}r\\ &= 0\end{aligned} \tag{37}$$

but the integrand of the left hand side changes sign at the node, and the theorem not applies in the rank $[0, \infty]$. In Ref. [9] and in the Fig. 1 of Ref. [15] the points for which the function φ changes its sign are shown.

Acknowledgements This work was funded by project no. BQU2001-0883, supported by the DGICYT of Spain.

References

1. Colle R, Salvetti O (1975) Theor Chim Acta 37:329
2. Colle R, Salvetti O (1979) Theor Chim Acta 53:55
3. Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785
4. Colle R, Salvetti O (1983) J Chem Phys 79:1404
5. Colle R, Salvetti O (1990) J Chem Phys 93:534
6. Pastor-Abia L, Pérez-Jiménez A, Pérez-Jordá A, Sancho-García J, San-Fabián E, Moscardó F (2004) Theor Chem Acc 111:1
7. Moscardó F, San-Fabián E (1991) Phys Rev A 44:1549
8. Malcom NOJ, McDouall JW (1998) Chem Phys Lett 282:121
9. San-Fabián E (1984) PhD thesis, Facultad de Ciencias, Universidad de Alicante, Alicante
10. Delgado-Barrio G, Moscardo F (1981) An Fis 77:63
11. Moscardó F, San-Fabián E (1986) Int J Quantum Chem 30:853
12. Tao J, Gori-Giorgi P, Perdew JP, McWeeny R (2001) Phys Rev A 63:032513
13. Moscardó F, Pérez-Jiménez AJ (1998) Int J Quantum Chem 67:143
14. Singh R, Massa L, Sahni V (1999) Phys Rev A 60:4135
15. Caratzoulas S, Knowles PJ (2000) Mol Phys 98:1811
16. Moscardó F, San-Fabián E (1991) Int J Quantum Chem 40:23
17. Salvetti O, Montagnani R (2001) Phys Rev A 63:052109
18. Jastrow R (1955) Phys Rev 98:1479
19. Bronshtein I, Semendyayev K (1998) Handbook of mathematics. Springer, Berlin Heidelberg New York
20. Soirat A, Flocco M, Massa L (1994) Int J Quantum Chem 49:291
21. Wigner E (1934) Phys Rev 46:1002
22. Moscardó F, Pérez-Jiménez AJ (1997) Int J Quantum Chem 61:313
23. Valdemoro C (1992) Phys Rev A 45:4462
24. Colmenero F, Valdemoro C (1992) Phys Rev A 47:979
25. Ehara M, Nakata M, Kou H, Yabuda K, Nakatsuji H (1999) J Chem Phys 305:483
26. Mazziotti D (1998) Phys Rev A 57:4219
27. Mazziotti D (1999) Phys Rev A 60:3618
28. Dunning THJ (1989) J Chem Phys 90:1007
29. Woon D, Dunning THJ (1994) J Chem Phys 100:2975
30. Slamet M, Sahni V (1995) Phys Rev A 51:2815